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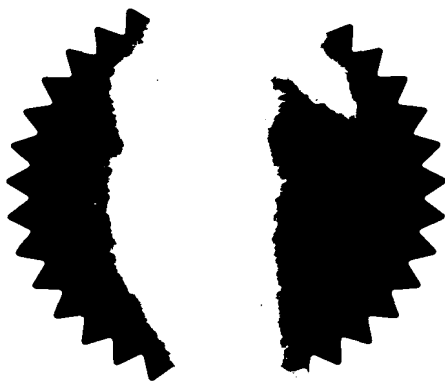
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Dated

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BRITISH TECHNOLOGY GROUP LIMITED
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COMPACTED BIOMATERIALS

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Description 15

Claim(s) 6

Abstract 1

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Date 30 MAY 1996

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COMPACTED BIOMATERIALS.

The present invention relates to novel composite materials, to a process for production of such materials and to their use as structural materials, particularly in prostheses but also in other non-physiological situations.

5 Hydroxyapatite (HA) reinforced high density polyethylene (PE) composite (HAPEX) was pioneered as a bone substitute by Bonfield et al. (see GB 2085461 B) who demonstrated that an optimum combination of mechanical and biological performance is produced by HA content in the region of 40 vol %. This amount of reinforcement was shown to result in a bone substitute with a stiffness and strength suitable for minor load
10 bearing applications. However, for major load bearing skeletal implants considerably higher stiffness and strength are required, comparable with the values associated with cortical bone.

 Molecular orientation in a polymer leads to a significant enhancement in the stiffness and strength along the orientation direction (I.M. Ward, "The preparation, structure
15 and properties of ultra-high modulus flexible polymers", Advances in Polymer Science, vol. 70, pp. 1-70, 1985).

 It is desirable to have methods for the production of suitable structural materials, and particularly bio-structural materials, with the purpose of achieving increased bio-compatible filler content, particularly HA content for higher bioactivity, and better
20 mechanical properties such as non-brittleness while having a load bearing capability.

 The present inventors have now provided such a method having the basic concept of combining polymeric fibres, preferably of polyolefins such as PE, with fillers, particularly biocompatible fillers such as HA, to produce structural materials, particularly bone analogues, by replacing the previously used isotropic polymer with polymeric fibre,
25 particularly high modulus polyolefin fibre such as polyethylene (HMPE) fibres, and compressing this mixture using hot compaction. Preferably the fibre is used as pieces of fibre in chopped fibre form.

 Hot compaction is a process which allows the production of large section polymeric products with substantial fibre morphology content, retaining to a large extent the high

stiffness and strength associated with fibres (see GB 2253420 and US Serial No.07/934,500 derived from PCT/GB92/00401), particularly high modulus fibres.

The present method is of particular interest in the fabrication of HA/PE composites having a fibre morphology matrix, using chopped HMPE fibres. The present inventors
 5 have further found, surprisingly, that such a material is amenable advantageously to extrusion, particularly hydrostatic extrusion, a technology never before attempted with hot compacted fibres. While the present method may be preferentially applied to such polymers, it may also be applied to other oriented polymers such as vinyls, polycsters, polyamides, polyetherketones and polyacetals such as vinyl chlorides, vinyl fluorides,
 10 vinylidene fluorides, PIIB, PEEK, polyoxymethylenes and all the other materials referred to as suitable for hot compaction use in PCT/GB92/00401.

Thus in a first aspect of the present invention there is provided a composite material comprising an inorganic filler material and a fibrous polymeric material characterised in that the fibrous material has areas of adjacent fibres fused together to form a network or
 15 continous matrix while retaining fibrous structure in the composite.

Preferably the fused fibres are oriented. Preferably the inorganic filler is a particulate filler. Examples of fillers include silicas, talc, mica, graphite, metal oxides, metal hydroxides and metal carbonates. Most preferably the inorganic filler is a biocompatible material, such as for example an apatite, eg. hydroxyapatite.

20 The composite material is preferably of extruded form and particularly of a hydrostatically extruded form.

Preferred composite materials of the invention have a flexural modulus between 7 and 30 GPa, preferably greater than 10 GPa, still more preferably having a flexural modulus greater than 12 GPa, most preferably greater than 15 GPa.

25 Preferred composite materials of the invention have a flexural strength between 50 and 150 Mpa, more preferably greater than 60 Mpa, still more preferably greater than 80 Mpa and most preferably greater than 100 MPa.

Preferred composite materials of the invention have a flexural ductility between 0.5 and 10 %, more preferably, between 0.5 and 7%, most preferably between 0.5 and
 30 4%.

Preferably the fibrous polymeric material is a polyolefin, preferably polypropylene

In a second aspect of the invention there is provided a method for producing a composite material from an inorganic filler material and a fibrous polymeric material including the steps of mixing and heating the filler material and fibrous polymeric material characterised in that it comprises (i) mixing the materials and maintaining the mixture at a contact pressure such that at least some of the fibres are in intimate contact with each other, (ii) heating the mixture so maintained at a temperature and for a time such as to melt no more than a part of the fibre surface area then (iii) compressing the heated mixture at a compaction pressure.

Preferably the part of the fibre surface area that melts is from 5 to 95% of the fibre surface area, more preferably from 5 to 50% of the surface area.

Preferably the material is cooled after compaction such that on cooling the melted part of the fibrous polymeric material forms a three dimensional matrix binding the fibrous material and filler material together. In the contact pressure maintaining step the mixture is preferably maintained at a temperature at least that which an extrapolation of the leading edge of the endotherm of the fibrous material measured by differential scanning calorimetry intersects the temperature axis.

20 Preferably the temperature at which the mixture is maintained is less than the peak temperature of melting of the polymer fibres as measured by differential scanning calorimetry.

The mixture is preferably maintained at a contact pressure of 0.5 to 4 MPa during step (i) and step (ii) prior to compressing at a compaction pressure; still more preferably between 0.5 and 2 MPa prior to compressing at a compaction pressure.

25 The material preferably comprises oriented polymer fibres, preferably in the form of continuous fibres that have been chopped into smaller lengths.

The temperature at which the mixture is maintained is preferably at between 1 and 10°C below the melting point of the polymeric material, more preferably between 1 and 5°C below the melting point of the polymeric material.

30 In a preferred method of the invention the compacted material produced in step (iii) is subjected to extrusion, more preferably hydrostatic extrusion. The product from step (iii)

or the extrusion step is advantageously powderized then reprocessed as in steps (i) to (iii). This reprocessing is preferably carried out by recompacting at a temperature of a few degrees centigrade lower than the first compaction in order to ensure that only the originally melted fraction is re-melted and the fibre morphology is maintained. A typical
 5 recompaction temperature is about 4°C less than the first melting temperature.

Preferably the reprocessed material is then subjected to extrusion, preferably hydrostatic extrusion.

The hydrostatic extrusion step is preferably performed by (iv) placing a billet of the material in contact with a die orifice while being surrounded by a fluid medium, (v)
 10 heating then fluid and the billet to a temperature below the melting point of the polymeric component of the material and (vi) applying pressure to the fluid such as to cause the billet to be extruded through the die.

Preferably the die is a convergent die, more preferably having an extrusion ratio of extruded product 3:1 or more, more preferably 7:1 or more and most preferably at least
 15 11:1.

Preferably the fluid used in the hydrostatic extrusion is an oil.

Preferably the compaction pressure used in step (iii) is from 5 to 1000MPa, more preferably 20 to 500 Mpa, and most preferably from 40 to 80MPa.

Preferably the polymer is a homo or co-polymer of a polyolefin, more preferably
 20 having a weight average molecular weight of 50,000 to 3,000,000 and still more preferably from 100,000 to 3,000,000 and most preferably 500,000 to 3,000,000.

The fibre is preferably gel or melt spun fibre.

25 The composites of the invention are preferably used in or as prostheses, and particularly as bone replacement prostheses.

The method and materials of the present invention will now be described by way of illustration only by reference to the following non-limiting Examples. Further embodiments falling within the scope of the invention will occur to those skilled in the art in the light of
 30 these.

EXAMPLES

EXPERIMENTAL

Materials

HA is a synthetic calcium phosphate ceramic $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})]$ supplied by Biotal Ltd., UK. Grade P88 was chosen for the present work, with $4.14 \mu\text{m}$ average size. Chopped HMPE fibres were supplied by Hoechst Celanese Research Co. (Summit, NJ, USA), from continuous fibres manufactured by SNIA Fibres (Cesano Maderno, Italy). Some samples also contained a third type of material, namely 40 vol % HA/60 vol % PE composite produced with the melt compounding technology, as seen in a previous publication. The polymer was Rigidex HM 4560 PX (BP Chemicals Ltd., UK) whilst the HA was P88 grade.

Table 1 gives the main parameter values characterising the PEs and HA used in this work.

METHODOLOGY

15 Preparation of Composites

The HA particles and chopped fibres were mixed at room temperature with a domestic appliance, namely a Braun Hand Blender MR 350 and the chopper HC accessory (Braun (UK) Ltd., London). This equipment was found particularly convenient because the handheld motor casing and the chopper are both axially aligned, allowing the blending to be carried out at an inclined angle while rolling the lower end on the bench. This procedure assisted the movement of the fibres inside the containers and avoided agglomeration. The chopper accessory was modified to improve efficiency, namely a) a second pair of blades was added midway along the shaft, b) the nylon bearings were replaced by ball bearings, and c) the plastic base was replaced by a heavier aluminium base.

Mixing of about 5g of chopped fibres plus the required amount of ILA was carried out for about 3 minutes using the three available motor speeds and rest periods in a reproducible sequence.

The composites were compacted in an aluminium mould placed in a hydraulic hot press. The mould produced samples of rectangular cross section and 150 x 10 mm L x W.

Maximum thickness was 8 mm. The temperature during compaction was monitored with a probe connected to an electronic thermometer. 5 mm of the sensing end of the probe could be inserted with a tight fit into holes bored at various points around the mould. The space between the hot plates of the press was shielded from the outside with Perspex sheets.

5 With these arrangements a predetermined moulding temperature (usually around 135°C) in the middle of the mould could be achieved within 0.2°C, whilst the gradient between the two ends of the mould was 0.5°C.

The blended material inside the mould was maintained at the predetermined temperature for 20 minutes under a small pressure (approximately 100psi = 0.69MPa) to ensure good thermal contact between the mould and the two hot plates of the press. The compression load was then increased rapidly to 9 tonne giving a compaction pressure of about 60MPa, followed by switching the heating off and water cooling of the hot press. The mould reached a temperature of 50°C in about 30 minutes, when it was left on a bench to cool down to room temperature before removing the sample.

Some samples were powderised to improve the HA distribution within the polymeric matrix. The powderising process included three stages a) crushing in a fly press, b) chopping with a Kenwood Chef Food Mixer fitted with the spice mill attachment (Kenwood Ltd., Havant, Hampshire, UK), and c) powderising proper in a Fritsch Pulverisette 14 Rotor-Speed Mill (Fritsch GmbH, Idar-Oberstein, Germany) using progressively finer sieves from 6 mm down to, when required, 80 μm . The Rotor-Speed Mill was fitted with a 12 knives stainless rotor and the speed used was 16,000 r.p.m.

Powderising could be readily achieved down to a 1 mm sieve. Finer sieves required considerable care owing to heat generation. The material to be fed into the Rotor-Speed mill was kept in a beaker, which was itself immersed in liquid nitrogen. However, no liquid nitrogen was poured into the machine.

After powderising, the material was re-compacted. At this stage it was necessary to re-melt the polyethylene fraction which melted during the first compaction, but without affecting the fraction with fibre morphology. This was achieved by re-compacting at 3°C to 4°C lower than the temperature used during the first compaction (the HMPE fibres melt at about 140°C, which compares with $\approx 130^\circ\text{C}$ for isotropic PE).

In some cases, composites were prepared in a somewhat different way,

namely the chopped HMPE fibres were blended with a mixture of HA and compacted, 40 vol % HA/60 vol % PE composite. The latter was prepared as seen in GB 2085461 B and was available in coarse powder form. The HA and compounded composite were blended in a Waring 8011G Rotary Blender (Waring Products Div., Dynamics Corporation of America, Connecticut, 06057, USA) fitted with the stainless steel mini container MC3. The mixing was carried out using a reproducible sequence of blending pulses (15 seconds), tapping and scrubbing the containers floor with a metal spatula. The powder thus obtained was compressed in a stainless steel mould placed in a hydraulic press. The procedure for this stage was similar to that followed for the production of compacted fibre composites, as seen above, except that the moulding temperature was 180°C and the samples were cylindrical rods 60 mm x 12 mm or 60 mm x 18 mm, L x diameter. For convenience this material will be referred to as "enriched" compounded composite (ECC).

The rods of "enriched" compounded composite were powderised as seen above and blended with the chopped HMPE fibres following a similar technique as used for the HA/chopped fibre system. The proportion of the various materials used was chosen such that the final mix achieved the predetermined HA content, while two thirds of the PE had fibre morphology.

Hydrostatic Extrusion

Details of the experimental procedure may be seen in Gibson and Ward (see
20 Example 2) and only a brief summary will be presented here.

The die used had a cone semiangle of 15° and the bore diameters were 1.8 mm, 2.5 mm or 3.5 mm, according to the extrusion ratio (ER) and the original dimensions of the compacted bars of composite to be extruded. Billets were machined from the bars with a 15° nose to create an initial pressure seal. At the end of the nose a constant diameter stub was also machined, which protruded a few millimetres through the die. A cable attached to the stub was used to drive a rotary potentiometer to provide a displacement signal which was recorded from the beginning of the extrusion (this was the first time that the HE process was monitored from its initial stages). A haul off load of 100 g was attached to the free end of the cable to ensure a firm drive of the rotary potentiometer. The back 3 mm of the billet was machined to a larger diameter to act as a plug and prevent the violent release

TABLE 1

MATERIAL CHARACTERIZATION

| | |
|---------------------------------------|---------|
| HA (P88) | |
| Density (g/cm ³) | 3.156 |
| Particle size (μm) | 4.14* |
| HMPE Fibre | |
| Density (g/cm ³) | 0.960 |
| \overline{M}_w | 130.000 |
| \overline{M}_n | 12.000 |
| DR | 30:1 |
| Diameters (μm) | 13 |
| Tensile modulus (GPa) | 40 |
| Tensile strength (GPa) | 1.3 |
| Fracture strain | 5% |
| Segment length of choopped fibre (mm) | 3.5 |
| Rigidex HM 4560XP | |
| Density (g/cm ³) | 0.945 |
| \overline{M}_w | 350.000 |
| \overline{M}_n | |
| Tensile modulus (GPa) | 0.68 |
| Tensile strength (MPa) | 23.5 |
| Fracture strain % | >300 |

* From ref. (8)

TABLE 2

FLEXURAL TEST PARAMETERS

| TEST | LOADING/ SUPPORTING RODS DIAMETER | GAUGE LENGTH+ | NOMINAL SAMPLE DIMENSIONS | | | | CROSSHEAD SPEED | PROPERTY CALCULATED AT STRAIN |
|-------------------|---|------------------|---------------------------|---------------------|---------------------|---------------|--------------------|-------------------------------------|
| | | | LENGTH | (mm) | | CROSS SECTION | | |
| | | | | RECTANGULAR BARS | CYLINDRICAL RODS | | | |
| | | | | | | | | |
| FM ₁₃₀ | 25/12 | 130 | 150 | 10 x 2 | | As Extruded | 2.0 | 0.03 |
| FM ₅₀ | 10/10 | 50 | 7.5 | | | | 0.5 | 0.03 |
| FS/FD | 10/10 | 50 | 7.5 | | | | 2.0 | - |

+ Distance between the supporting rods

TABLE 3
SIMPLE BEAM THEORY FORMULAE FOR
THREE POINT BENDING

| | RECTANGULAR BARS | CYLINDRICAL RODS |
|----------------|---|---|
| FM | $\frac{1}{4} \frac{WL^3}{\delta b d^3}$ | $\frac{4}{3} \frac{WL^3}{\pi \delta D^3}$ |
| FS | $\frac{3}{2} \frac{WL}{b d^2}$ | $\frac{8WL}{\pi d^3}$ |
| MAXIMUM STRAIN | $\frac{\delta}{L^2}$ | $\frac{6D\delta}{L^2}$ |
| SYMBOLS | <p>W = Load</p> <p>δ = Deflection</p> <p>L = Gauge Length</p> <p>d = Sample Thickness</p> <p>b = Sample Width</p> | <p>W = Load</p> <p>δ = Deflection</p> <p>L = Gauge Length</p> <p>d = Diameter of Overall Sample</p> <p>D = Diameter of Gauge Length</p> |

Example 1: Hydroxyapatite/High Modulus Polyethylene fibre composite.

HA particles and chopped HMPE fibres were mixed at room temperature with a modified domestic hand blender. The composites were compacted in an aluminium mould placed in a hydraulic hot press with preliminary experiments showing that compaction temperatures of between 137.0°C and 138.0°C are adequate to melt a small proportion of the fibre surface, as described in GB 2253420, and form a continuous network of re-crystallized PE binding the fibres and the HA particles together

Some samples were powderized after compaction with the purpose of improving the HIA distribution within the polymeric matrix. The material was re-compacted at about 3.0°C-4.0°C lower than the first compaction temperature, ensuring the re-melting of the PE fraction melted during the first compaction, but without affecting the fraction retaining the fibre morphology (the HMPE fibres melt at $\approx 140^\circ\text{C}$, which compares with $\approx 130^\circ\text{C}$ for the re-crystallized PE).

In some cases the composites were prepared in a somewhat different way, namely by blending the HMPE chopped fibres with a mixture of HA and HAPEX (40 vol % HA)]. This mixture is referred to as "enriched" HIAPEX. The proportions of the various materials used were chosen such that the final mix had the predetermined HA content, with two-thirds of the PE having fibre morphology.

20 Example 2: Hydrostatically extruded hot compacted composite

The hydrostatic extrusion process [A.G. Gibson and I.M. Ward, "Hydrostatic extrusion of linear polyethylene: effects of molecular weight and product diameter", J. Polym. Sci., Polym. Phys. Ed., vol. 16, pp. 2015-3030, 1978] used a billet of the composite surrounded by a fluid which was heated up below its melting point. The billet was made to pass through a convergent die by the application of a back pressure to the fluid. The extrusion ratio (ER) is defined as the ratio of the cross section area of the billet to that of the die bore. It was found that powderizing and re-compaction were necessary requirements for the successful hydrostatic extrusion of HA/chopped HMPE fibre composites.

The mechanical properties of the composites were assessed in three point bending. Three measurements were undertaken, namely flexural modulus (FM), flexural

strength (IS) and flexural ductility (FD). The term "ductility" refers to the maximum strain (in %) in the sample at the deflection producing failure.

Properties:

Tables 3a and 3b give the main flexural properties of IIA/chopped HMPE fibre composites. For comparison, some results obtained with other materials are also included. All the hydrostatically extruded composites achieve the levels of stiffness and strength associated with cortical bone. On the other hand, none of the composites without hydrostatic extrusion possess properties comparable to the biological tissue.

When comparing the system without hydrostatic extrusion, Table 1a shows that the properties of HAPEX are broadly matched by the properties of HA/chopped fibre composites. However, after hydrostatic extrusion these systems are distinctly superior to extruded IIAPEX (Table 3b).

SEM observations with polished samples showed that HAPEX has a highly homogeneous distribution of HA particles in the polymeric matrix, whereas HA/chopped fibre composites have regions with varying degrees of HA content. Powderizing and re-compaction of the HA/chopped fibre systems significantly improved their IIA distribution and these stages were required for successful hydrostatic extrusion, as noted above.

Table 3a shows that powderizing and recompaction of HA/chopped fibre composites are accompanied by a reduction in their stiffness and strength. This can be attributed to damage of the fibre morphology taking place during the powderizing stage, as shown by DSC studies, which also reveal that a high melting point morphology (fibre morphology) is re-established during the hydrostatic extrusion process, accounting for the superior properties of these systems (Table 3b).

Thus these results show that hydrostatic extrusion of hot compacted HA/chopped HMPE fibre composites which have been powderized and re-compacted provides the highest stiffness and strength yet encountered with HA/PE bone substitute material, fully comparable with the values associated with cortical bone.

Table 6. Flexural properties of extruded and non-extruded HA/chopped IIMPE fibre composites of the invention.

a) Non-extruded (Example 1)

| HA content [vol %] | Powderizing [mm] | FM [GPa] | FS [MPa] | FD [%] |
|------------------------|---------------------|-------------|-------------|------------|
| Cortical bone | - | 7-30 | 50-150 | 0.5-3.0 |
| HAPEX | - | 4.7 | 32 | 1.4 |
| 0 | - 0.5 | 3.9 2.4 | 54 19 | 4.2 0.9 |
| 20 | - 0.5 | 5.8 3.6 | 49 41 | 2.8 2.7 |
| 30* | - 0.5 | 5.5 4.2 | 47 38 | 2.3 1.9 |

b) Hydrostatically extruded (Example 2).

| HA content [vol %] | ER | FM [GPa] | FS [MPa] | FD [%] |
|------------------------|--------------------|---------------------|------------------|-------------------|
| HAPEX [8] | 8:1 | 8.8 | 81 | 5.5 |
| 0 | 4:1 7:1 | 6.9 12.7 | 88 103 | 6.0 3.9 |
| 20 | 7:1 | 15.2 | 119 | 3.6 |
| 30 | 4:1 7:1 11:1 | 9.3 15.5 19.5 | 86 104 117 | 3.4 3.0 2.8 |
| 30* | 4:1 7:1 | 9.0 11.9 | 75 87 | 3.6 3.3 |
| 40 | 4:1 7:1 | 10.8 14.1 | 86 97 | 3.8 3.8 |
| 50* | 7:1 11:1 | 12.4 13.5 | 72 67 | 2.8 1.6 |

* For these systems the HA was incorporated as "enriched" HAPEX.

CLAIMS.

1. A composite material comprising an inorganic filler material and a fibrous polymeric material characterised in that the fibrous material has areas of adjacent fibres fused together to form a network or continuous matrix while retaining fibrous structure in the composite.
2. A composite material as claimed in claim 1 wherein the fused fibres are oriented.
3. A composite material as claimed in claim 1 or 2 wherein the inorganic filler is a particulate filler.
4. A composite material as claimed in any one of claims 1 to 3 wherein the filler is selected from talc, mica, graphite, metal oxides, metal hydroxides and carbonates.
5. A composite material as claimed in any one of claims 1 to 4 wherein the inorganic filler is a biocompatible material.
6. A composite material as claimed in claim 5 wherein the biocompatible material is an apatite.
7. A composite material as claimed in claim 6 wherein the apatite is hydroxyapatite.
8. A composite material as claimed in any one of claims 1 to 7 wherein the material is of extruded form.
9. A composite material as claimed in claim 8 wherein the material is in hydrostatically extruded form.
10. A composite material as claimed in any one of claims 1 to 9 having flexural modulus between 7 and 30 GPa.

11. A composite material as claimed in claim 10 having flexural modulus greater than 10 GPa.
12. A composite material as claimed in claim 10 having a flexural modulus greater than 12 GPa.
- 5 13. A composite material as claimed in claim 10 having a flexural modulus greater than 15 GPa.
14. A composite material as claimed in any one of claims 1 to 13 having a flexural strength between 50 and 150 MPa.
15. A composite material as claimed in claim 14 having a flexural strength greater than
10 60 MPa.
16. A composite material as claimed in claim 14 having a flexural strength greater than 80 MPa.
17. A composite material as claimed in claim 14 having a flexural strength greater than 100 MPa.
- 15 18. A composite material as claimed in any one of claims 1 to 17 having a flexural ductility between 0.5 and 10 %.
19. A composite material as claimed in claim 18 having a flexural ductility between 0.5 and 7%.
20. A composite material as claimed in claim 19 having a flexural ductility between
20 0.5 and 4%.

21. A composite material as claimed in any one of the preceding claims wherein the fibrous polymeric material is a polyolefin.
22. A composite material as claimed in claim 21 wherein the polyolefin is polyethylene.
23. A composite material as claimed in claim 21 wherein the polyethylene is of high
5 modulus.
24. A method for producing a composite material from an inorganic filler material and a fibrous polymeric material including the steps of mixing and heating the filler material and fibrous polymeric material characterised in that it comprises (i) mixing the materials
10 in intimate contact with each other, (ii) heating the mixture so maintained at a temperature and for a time such as to melt no more than a part of the fibre surface area then (iii) compressing the heated mixture at a compaction pressure.
25. A method as claimed in claim 24 wherein the part of the fibre surface area that melts is from 5 to 95% of the fibre surface area.
- 15 26. A method as claimed in claim 25 wherein the part of the fibre surface area is from 5 to 50% of the surface area.
27. A method as claimed in claim 24 wherein the compressed mixture is cooled such that on cooling the melted part of the fibrous polymeric material forms a three dimensional matrix binding the fibrous material and filler material together.
- 20 28. A method as claimed in any one of claims 24 to 27 wherein the mixture is maintained at a temperature at least that which an extrapolation of the leading edge of the endotherm of the fibrous material measured by differential scanning calorimetry intersects the temperature axis.

29. A method as claimed in claim 28 wherein the temperature at which the mixture is maintained is less than the peak temperature of melting of the polymer fibres as measured by differential scanning calorimetry.
30. A method as claimed in any one of claims 24 to 29 wherein the mixture is
5 maintained at 0.5 to 4 MPa during step (i) and step (ii) prior to compressing at a compaction pressure.
31. A method as claimed in claim 30 wherein the mixture is maintained at between 0.5 and 2 MPa prior to compressing at a compaction pressure.
32. A method as claimed in any one of claims 24 to 31 wherein the fibrous material
10 comprises oriented polymer fibres.
33. A method as claimed in any one of claims 24 to 32 wherein the fibres are in the form of continuous fibres that have been chopped into smaller lengths.
34. A method as claimed in any one of claims 24 to 33 wherein the temperature at
15 which the mixture is maintained is between 1 and 10°C below the melting point of the polymeric material.
35. A method as claimed in claim 34 wherein the temperature is between 1 and 5°C below the melting point of the polymeric material.
36. A method as claimed in any one of claims 24 to 35 wherein the compacted material
20 produced in step (iii) is subjected to extrusion.
37. A method as claimed in claim 36 wherein the extrusion step is carried out by hydrostatic extrusion.

38. A method as claimed in claim 36 or 37 wherein the product from step (iii) or the extrusion step is powderized then reprocessed as in steps (i) to (iii).

39. A method as claimed in claim 38 wherein the reprocessed material is then subjected to extrusion.

5 40. A method as claimed in claim 39 wherein the extrusion is hydrostatic extrusion.

41. A method as claimed in claim 36 or claim 40 wherein the hydrostatic extrusion step is performed by (iv) placing a billet of the material in contact with a die orifice while being surrounded by a fluid medium, (v) heating then fluid and the billet to a temperature below the melting point of the polymeric component of the material, (vi) applying pressure to the fluid such as to cause the billet to be extruded through the die.

42. A method as claimed in claim 41 wherein the die is a convergent die.

43. A method as claimed in claim 41 or 42 wherein the extrusion ratio of the extruded product is 3:1 or more.

44. A method as claimed in claim 43 wherein the extrusion ratio is 7:1 or more.

15 45. A method as claimed in claim 44 wherein the extrusion ratio is at least 11:1.

46. A method as claimed in any one of claims 42 to 45 wherein the fluid is an oil.

47. A method as claimed in any one of claims 24 to 46 wherein the compaction pressure used in step (iii) is from 5 to 1000MPa.

48. A method as claimed in claim 47 wherein the compaction pressure used in step (iii)
20 is from 20 to 500 Mpa.

49. A method as claimed in claim 48 wherein the compaction pressure is from 40 to 80MPa.
50. A composite or method as claimed in any one of claims 1 to 49 wherein the polymer is a homo or co-polymer of a polyolefin.
- 5 51. A composite or method as claimed in claim 50 wherein the polymer has a weight average molecular weight of 50,000 to 3,000,000.
52. A composite or method as claimed in claim 51 wherein the polymer has a weight average molecular weight of 100,000 to 3,000,000.
53. A composite or method as claimed in claim 51 wherein the polymer has a weight
10 average molecular weight of 500,000 to 3,000,000.
54. A composite or method as claimed in any one of claims 47 to 53 wherein the fibre is gel or melt spun fibre.
55. A structural material comprising a composite as claimed in or provided by a method
15 as claimed in any one of the preceding claims.
55. A prosthesis comprising a material as claimed in claim 55.

ABSTRACT

COMPACTED BIOMATERIALS

A composite material comprising an inorganic filler material and a fibrous polymeric material characterised in that the fibrous material has areas of adjacent fibres fused together
5 to form a network or continuous matrix while retaining fibrous structure in the composite.

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